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RGO/CNF/PANI AS AN EFFECTIVE ADSORBENT FOR THE ADSORPTION OF URANIUM FROM AQUEOUS SOLUTION

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ABSTRACT

In this paper, we present a recent study in the adsorption of uranium from an aquatic environment by reduced graphene oxide - $Cu_{0.5}Ni_{0.5}Fe_2O_4$ ferrite – polyaniline (RGO/CNF/PANI) composite. Uranium concentration was carried out by batch techniques. The effect of pH, contact time, concentration of equilibrium state and reusability on uranium adsorption capacity have been studied. The adsorption process was accomplished within 240 min and could be well described by the pseudo-second-order model. The adsorption isotherm agrees well with the Langmuir model, having a maximum adsorption capacity of 2000 mg/g, at pH = 5 and 25 ^oC. The RGO/CNF/PANI materials could be a promising absorbent for removing U (VI) in aqueous solution because of their high adsorption capacity and convenient magnetic separation.

Keywords: $Cu_{0.5}Ni_{0.5}Fe_2O_4$, polyaniline, reduced graphene oxide, uranium, adsorption.

1. INTRODUCTION

With fast improvement of atomic technologies, worries about wastewater treatment have prompted an incredible number of examinations to remove uranium squander from water. The radioactivity and toxicity of uranium present serious hazards to human beings [1]. There are different techniques to treat uranium from watery solutions, for example chemical precipitation, layer dialysis, dissolvable extraction, buoyancy and adsorption [2]. In those techniques, adsorption is presumably the most well-known technique. Advancement of adsorbents with high adsorption capacity, quick adsorption and simple detachment has gotten impressive enthusiasm for late years [3, 4].

The magnetic-based nanomaterials are superior adsorbent because it could be easily separated from wastewater [3]. Graphene oxide (GO) -polyaniline(PANI) composites are appealing materials with high uranium adsorption [5]. But the GO-PANI composites are hard to isolate aqueous solution from after the adsorption process, which may increase the cost of industrial application. Therefore, the composite material which consists of magnetic nanoparticles, GO and PANI, has promised an effective adsorbent [6].

In our previous reports, reduced graphene oxide - $Cu_{0.5}Ni_{0.5}Fe_2O_4$ ferrite – polyaniline (RGO/CNF/PANI) composite have been prepared by a three-step method [7]. The purpose of this work is to investigate the feasibility of adsorption of uranium (VI) by this material. The uranium (VI) adsorption was analyzed as functions of *pH*, contact time, concentrations and reusability.

2. EXPERIMENTAL

Analytical grade chemicals were used. Sodium hydroxide (NaOH, 99 %), nitric acid (HNO3, 65 %) and hydrochloric acid (HCl, 37 %) and uranyl nitrate hexahydrate ($UO_2(NO_3)_2.6H_2O$, 99 %) were supplied by Sigma-Aldrich company.

A batch technique was carried out to study the adsorption of U (VI) from aqueous solutions by RGO/CNF/PANI. All aqueous solutions using in adsorption experiments were prepared by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ in deionized water. All the adsorption experiments were performed at 25 ^oC and 20 mg of adsorbent. After the adsorption reached the equilibrium, the adsorbent was isolated by a magnet. It took a few minutes to separate this suspension from solutions. Then, the samples were filtered and the uranium concentration of the effluent was measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500). The effect of *pH* on adsorption was studied using a 400 mL (50 mg/L uranium) solution, a contact time of 240 min. The *pH* values ranging from 2 to 10 were adjusted by adding 0.1 mol/L NaOH or 0.1 mol/L HNO_3 solutions. The effect of contact time on adsorption capacity was studied at $V_{solution}$ = 400 mL, 50 mg/L uranium solution and *pH* = 5. The contact time was varied from 15 min to 360 min. In adsorption equilibrium isotherm studies, the initial concentrations of uranium were varied and the other parameters were kept constant ($V_{solution}$ = 400 mL, contact time = 240 min and *pH* = 5).

The amount of uranium adsorbed per unit mass of the adsorbent was calculated according to the following equation:

$$Q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where Q_e (mg/g) is the adsorption capacity, C_o and C_e (mg/L) are the concentrations of the uranium at initial and equilibrium states, respectively, m is the weight of sorbent (g), and V is the volume of the solution (L).

The regeneration–reuse studies were performed in six cycles. In each cycle, 20 mg adsorbent was mixed in 400 mL uranyl solution (50 mg/L). Adsorption of U (VI) was carried out at *pH* = 5, contact time = 240 min and 25 ^oC. After adsorption experiment, derived sample of U(VI) laden RGO-CNF-PANI composites were mixed with 0.1 mol/L HCl for 2 h at 25 ^oC. The composites were separated by a magnet.The recovered composite materials were washed thoroughly a few times with distilled water and dried at 50 ^oC. The adsorption efficiency in each cycle was calculated from the amount of uranium adsorbed on the adsorbents and the initial amount of uranium.

3. RESULTS AND DISSCUSION

3.1. The effect of solution *pH*

The impact of *pH* on the amount of uranium adsorbed on the RGO/CNF/PANI composite for U (VI) is represented in Fig. 1. The amount of uranium is increments when the pH increase from 2 to 5. As the pH value was consistently expanded from 5 to 10, the amount of U(VI)

decreases. This result shows that the sorption capacity of RGO/CNF/PANI for U (VI) is best at *pH* = 5. In acidic conditions, U (VI) is available as UO_2^{2+} and the sorption is low a result of the competition of H^+ ions for the coupling sites of the adsorbents. The concentrations of hydroxyl,carbonate and bicarbonate anions expanded alongside *pH* level. Therefore, the uranyl ions form stable complexes with hydroxyl and carbonate anions, bringing about a dramatic diminishing in adsorption capacity [8]. At *pH* > 5, the surface charge of sorbents became more negative and uranium is present as anionic species such as $[UO_2(OH)_3]^-$, $[UO_2(OH)_4]^{2-}$… The repulsion between uranium anions and sorbents with surface negative charges resulted in the drop of U(VI) sorption [13].

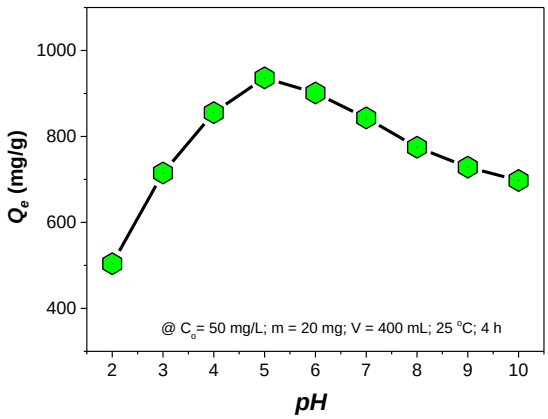


Figure 1. Effect of pH on adsorption of uranium.

3.2. The effect of contact time

Fig. 2 introduces the amount of uranium adsorption of the RGO/CNF/PANI composite as an element of contact time. There are two distinctive stages in this adsorption process, the initial process completing in around 240 min followed by a moderate and peripheral take-up stretching out to 360 min. The results of the adsorption experiments show that this nanocompositeis effective in decreasing the uranium concentration in the effluent.

A most extreme of 93.64 % diminish from the initial concentration of 50 mg/L is seen at 240 min of contact time. To guarantee that equilibrium was built up for each situation, a contact time of 240 min was chosen for all adsorption experiments. This contact time is similar to some other studies, but has a lower adsorption capacity [13, 15, 18, 19]. Compared to Shao et al.'s research (48 h of contact time), this value is much smaller [5].

The adsorption data were dealt with as indicated by the pseudo-first-order or pseudo-second-order kinetic equation [9] to research the controlling mechanism of the adsorption process. As observed from Fig. 3, since the higher correlation coefficient for the pseudo-second-order kinetics model is found to be closer to unity than that for the pseudo-first-order kinetics model. Moreover, the amount of uranium calculated by the pseudo-second-order kinetic equation is near the experimental values. It can be inferred that the sorption kinetics of uranium (VI) can be explained well in terms of the pseudo-second-order kinetic model for the RGO/CNF/PANI adsorbents.

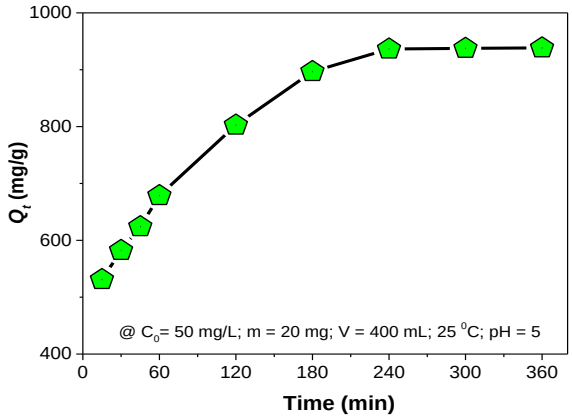


Figure 2. Effect of contact time on uranium adsorption.

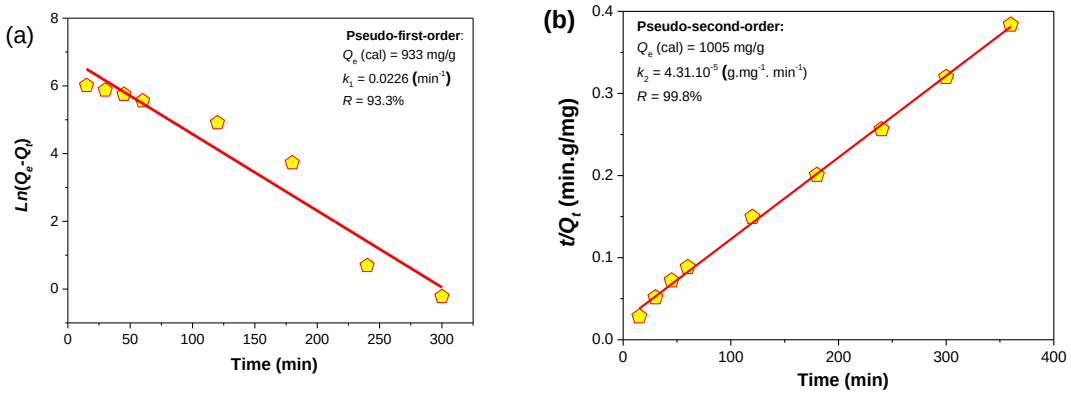


Figure 3. Pseudo-first (a) and second-order (b) plots for the adsorption of uranium.

3.3. Adsorption isotherms of uranium

The amount of uranium adsorbed on RGO/CNF/PANI nanocomposites versus the equilibrium concentration of U (VI) in the aqueous solution is plotted in Fig. 4.

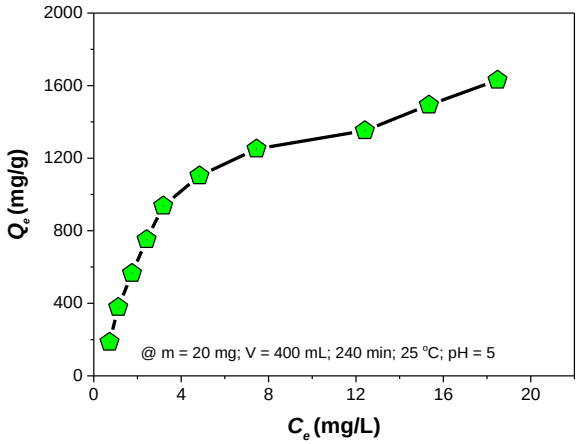


Figure 4. Effect of equilibrium uranium on the adsorption on RGO/CNF/PANI.

Obviously, increasing the uranium concentrations involves an increase in the uptake of uranium. The sorption isotherm gives the most important information, as it indicates how the sorbent molecules are distributed between the solid and the liquid phases when the sorption process reaches an equilibrium state. The removal of uranium in the presence of materials can be alloted to the interaction between material surface and uranium species present in solution. Under our experimental conditions, the amount of uranium loading onto the nanocomposite was found to be saturated at roughly 1604 mg/g.

To understand the adsorption behavior, the adsorption equilibrium data have been analyzed using various isotherm models, such as the Langmuir and the Freundlich models [10].

The Langmuir equation is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_L Q_m} \tag{2}$$

where Q_m (mg/g) is the Langmuir monolayer sorption capacity; C_e (mg/L) is the equilibrium concentration; Q_e (mg/g) is the adsorbed amount at equilibrium time; K_L is the Langmuir equilibrium constant.

The formula of Freundlich isotherm is :

$$\ln\ Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

K_F and n are the Freundlich constants related to the sorption capacity and sorption intensity, respectively.

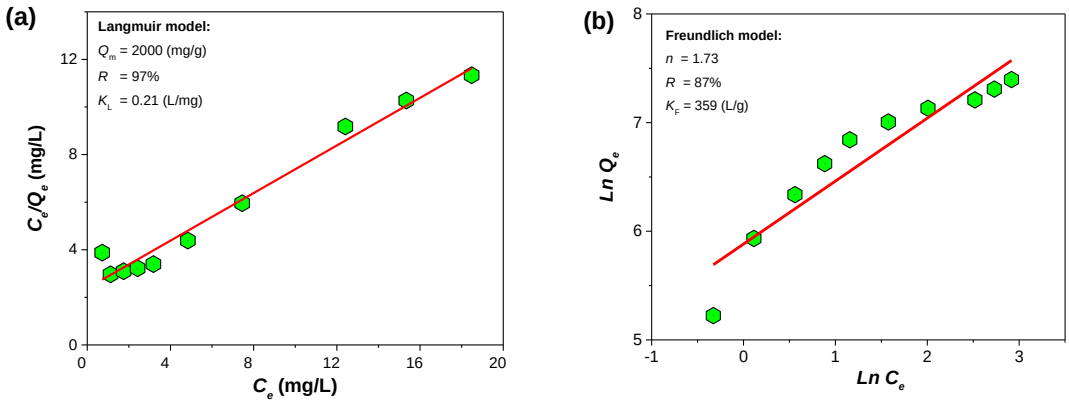
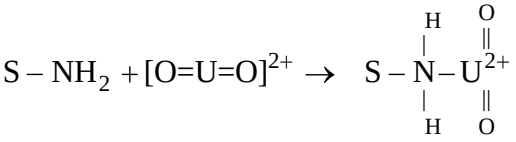


Figure 5. The sorption isotherms for the removal of uranium: Langmuir (a), Freundlich (b).

Plots of Langmuir, Freundlich models representing uranium adsorption are delineated in Fig. 5. In light of the high correlation coefficient values, the Langmuir isotherm is most reasonable to characterize the uranium adsorption behavior of RGO/CNF/PANI materials. The Langmuir model shows that uranium is adsorbed by particular locales of RGO/CNF/PANI and structures a monolayer. This additionally demonstrates the homogeneity of active sites on the surface of RGO/CNF/PANI. The maximum adsorption capacity of RGO/CNF/PANI is around 2000 mg/g for uranium at 25 ^{o}C. The adsorption capacity of the RGO/CNF/PANI composite is higher than some different adsorbents (Table 1).

The RGO/CNF/PANI materials have some kind of sorption centers (on ferrite particles due to nano sizes), sorption sites (on RGO due to its high specific surface area or RGO – ferrite intereaction). Moreover, this material has many complex surface groups such as S-NH_2, S=NH, S- COOH (where S is surface). These complex groups interact with uranium ions through electrostatic or hydrogen bond [5]. Thus, it makes increasing the adsorption capacity of this adsorbent.



(4)

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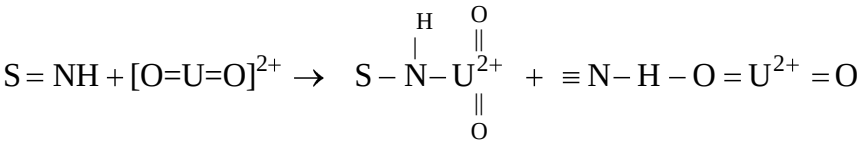

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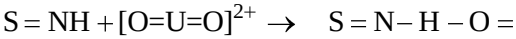

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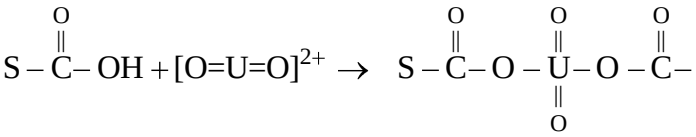

(8)

*Table 1.*Adsorption capacity of different adsorbents for uranium(VI).

Adsorbents	Capacity (mg/g)	Contact time (h)	*pH*	Ref
$Cu_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles	56	2	7	[11]
Fe_3O_4@TiO_2 core-shell	91	4	6	[19]
RGO/Fe_3O_4	97	1	7	[14]
Fe_3O_4@SiO_2-AO	119	24	7	[16]
Fe_3O_4-Oxine	125	4	7	[18]
$CoFe_2O_4$ hollow	170	3	6	[10]
$CoFe_2O_4$/Graphene	227	4	6	[13]
RGO/$Cu_{0.5}Ni_{0.5}Fe_2O_4$	256	4	6	[12]
Graphene oxide sheets	299	4	4	[15]
Fe^0/PANI/Graphene	350	0.5	5.5	[8]
RGO/$Zn_{0.5}Ni_{0.5}Fe_2O_4$/PANI	1885	4	5	[6]
PANI/GO	1960	48	6-7	[5]
RGO/$Cu_{0.5}Ni_{0.5}Fe_2O_4$/PANI	2000	4	5	This work
Zero-valent iron nanoparticles	8173	1	5	[17]

3.4. The regeneration–reuse studies

To assess the reusability of the adsorbent, the adsorption–desorption experiments was repeated six cycles. Fig. 6 presents the percentage of adsorption as a function of cycle number. After six cycles, the adsorption percentage decreased from 93.6 % to 91.5 %. After adsorption process, a few parts of the uranyl ions permeating into inner RGO/CNF/PANI structures to form stable complexes [9]. Therefore the adsorption percentage reduced gradually as the number of cycles increased. This percentage decreased slightly so the results may enhance the economy of the adsorption process. Similar results were also reported for U(VI) reusability study [5, 10, 18, 19]. This outcome indicates that the composite materials could be utilized effectively in a genuine wastewater treatment.

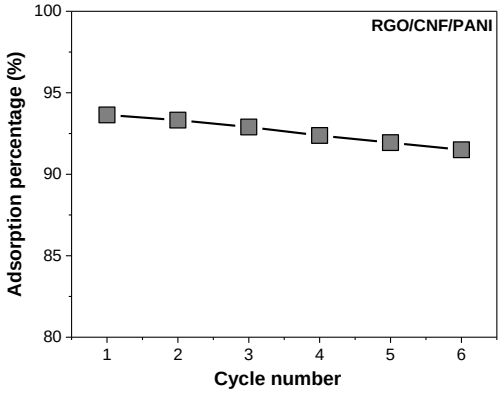

Figure 6. Recycling of RGO/CNF/PANI for the removal of uranium.

4. CONCLUSION

In conclusion, the RGO/CNF/PANI exhibits as an effective adsorbent in removing uranium (VI) from aqueous solution in view of their easily magnetic separation and high adsorption capacity. The adsorption process is *pH*-dependent with maximum adsorption at *pH* = 5. The adsorption of uranium process onto RGO/CNF/PANI nanocomposites were accomplished with adsorption equilibration at 240 min. The pseudo-second-order model and Langmuir isotherm were well fitted to explain the adsorption of uranium. The adsorption capacity of uranium with the RGO/CNF/PANI composite was 2000 mg/g at *pH* = 5 and 25 ^{o}C.

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